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Review is made of the feedback and gain enhancemnt mechanisms unique to microdroplets. In particular, the growth of stimulated Raman scattering is considered in the presence of two-photon absorption as well as the usual optical losses inside the droplet because of scattering and leakage out of the droplet cavity.

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CHARACTERISTICS AND APPLICATIONS OF STIMULATED RAMAN SCATTERING IN MICRODROPLETS

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In a mirrorless optical cell, the growth of the stimulated Raman scattering (SRS) is generally treated without optical feedback, and with the standard one-dimensional nonlinear wave equations that involve spatially overlapping waves along the copropagation direction [1]. A liquid droplet with radius a (larger than the wavelength) has three unique features. First, when a plane wave is incident on the droplet, the internal input-laser intensity I_{in} (at frequency ω_{in}) is concentrated in a localized region along the principal diameter (see Fig. 1) just within the droplet shadow face with ≈ 100X enhancement [2]. Second, some of the spontaneous Raman radiation is trapped by the droplet and circulates around the droplet rim because the droplet acts as a high-Q optical cavity at specific wavelengths within the Raman gain profile. These discrete wavelengths correspond to morphology-dependent resonances (MDR's) of a sphere which are characterized by a and the ratio of the indices of refraction of the liquid and of the surrounding medium. Those Raman waves that are on MDR's can be envisioned as two counterpropagating waves circulating just within the droplet rim and centered at $\omega_{1S} = \omega_{in} - \omega_{vib}$, where ω_{vib} is the molecular vibrational frequency (see Fig. 1). The spatial distribution of the MDR's is determined by three indices: (1) the mode order which specifies the number of peaks between $0 \le r \le a$ in the angle-averaged internal intensity distribution; (2) the mode number which is equal to twice the number of peaks in the internal intensity distribution around the droplet equator; and (3) the azimuthal mode index [3]. Third, the spontaneous-Raman transition rates, analogous to the fluorescence transition rates, can be enhanced if the Raman radiation couples to the discrete MDR's [4]. Consequently, the Raman scattering cross section or Raman gain is highly dependent on the location of the molecule within the droplet. For example, if the molecule is at the MDR intensity maximum (or minimum), the effective Raman cross section is increased (or decreased) [4,5]. Sharp peaks superimposed on the spontaneous Raman profile have been observed for spheres [6] and cylinders [7]. Sharp peaks in the SRS spectrum of diesel fuel droplets are shown in Fig. 2.

Significant decrease of the SRS threshold in microdroplets results from the combined effects of I_{in} concentration, optical feedback at MDR's, and enhanced Raman gain for molecules that have a good spatial overlap with MDR's. The SRS threshold is reached whenever the Raman gain at the localized region of intense I_{in} exceeds the round-trip loss (see Fig. 1). The SRS gain need not be provided by I_{in}. For most liquids, the spontaneous-Brillouin cross section is larger than the spontaneous-Raman cross section. Simultaneously recorded temporal profiles of the stimulated Brillouin scattering (SBS) and SRS reveals that the first SBS pulse always occurs earlier than the first SRS pulse, consistent with the fact that the Brillouin gain is larger than the Raman gain [8]. Even though the SBS intensity is less than I_{in}, the

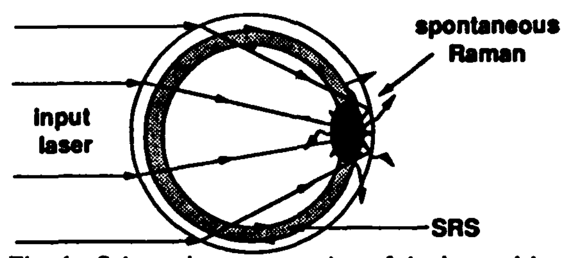

Fig. 1. Schematic representation of the internal intensity distributions within a fuel droplet. The shaded disk (just within the droplet shadow face) indicates the region of high I_{in}. The generated SRS wave is indicated by the shaded ring just within the droplet rim.

SRS can be pumped more efficiently by SBS than by I_{in}, because of the favorable spatial overlap between the SBS MDR and the SRS MDR [8]. The intensity depletion of SBS by pumping SRS is demonstrated by the temporal correlation of the SBS and SRS pulses; i.e., the minimum of the n-th SBS pulse occurs at the maximum of the n-th SRS pulse [8].

There are different sources of loss for the first-order Stokes SRS intensity I_{1S}: (1) radiation leakage from an ideal droplet, depending on the Q-value of the MDR; (2) radiation leakage from a perturbed droplet, e.g., with ripples on the surface and/or with inhomogeneous index of refraction inside the droplet [9]; (3) avoidable one-photon absorption (OPA); (4) possible nondegenerate two-photon absorption (TPA) involving one Raman photon and one input-laser photon as well as degenerate TPA involving two Raman photons [10]; and (5) intensity depletion because of I_{1S} pumping another first-order Stokes SRS, with intensity I_{2S}, centered at $\omega_{2S} = \omega_{in} - 2\omega_{vib}$ (see Fig. 1). Cascade pumping of SRS up to the twenty-first order Stokes SRS has been observed in CCl_4 droplets [11]. Even though the intensity of various orders of Stokes SRS is lower than I_{in}, spatial overlap between the I_{1S} MDR and the I_{2S} MDR is more favorable than the spatial overlap between the I_{1S} MDR and the localized region with intense I_{in} (see Fig. 1).

The detected SRS is due to the leakage of I_{1S}. The angular distribution of I_{1S} that is supported by many MDR's is essentially isotropic. However, at low I_{in} when I_{1S} is supported by only one MDR, the angular distribution exhibits fine structure, where the number of peaks corresponds to twice the MDR mode number [12]. The existence of fine structure in the angular distribution of I_{1S} implies that the two counterpropagating I_{1S} waves are phase coherent and form a stationary standing wave pattern around the droplet equator.

A flowing droplet is perturbed by inertial forces. The spherical droplet acquires the shape of an oblate spheroid with a small distortion amplitude ≈ 10^{-3}a. Again, at low I_{in} when the SRS is supported by one MDR of an ideal sphere, the SRS spectrum consists of several frequency split peaks which are spaced by ≈ 0.06 cm^{-1}, consistent with the perturbation theory prediction that the MDR's azimuthal degeneracy is lifted, when the droplet slightly distorts to a spheroid [9].

OPA loss at ω_{1S} may be diminished by selecting an ω_{in} so that ω_{1S} is outside the absorption band. For example, ω_{in} from a dye laser has to be shifted to 17699 cm^{-1} (corresponding to 565 nm) in order to minimize the OPA in diesel fuel droplets at ω_{1S} = 14749 cm^{-1}. Unavoidable amounts of OPA still exist in the diesel fuel droplets. Consequently, compared with a transparent droplet, OPA increases the

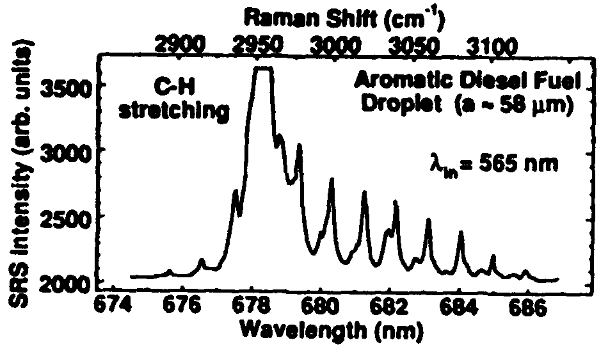

Fig. 2. SRS spectra from aromatic diesel fuel droplets. The peak of the C-H stretching mode at 678.5 nm is truncated in order to emphasize the MDR related peaks in the wings of the spectrum.

SRS threshold for diesel fuel droplets and causes the Q-value of the MDR providing the necessary feedback for the SRS process to be lower than the Q-value associated with only MDR-related leakage of a transparent droplet.

TPA effects may be unavoidable, particularly for large organic molecules with two-photon allowed transitions in the near UV. Figure 3 is a schematic of the dominant linear and nonlinear processes occuring within the droplet equatorial plane. The growth and decay of I_{1S}, as it circulates in the ϕ-direction within the droplet equatorial plane, can be expressed as [10,13]:

$$\frac{dI_{1S}}{a\,d\phi} = \left[(G - \beta_{in\text{-}1S}) I_{in} - \beta_{1S\text{-}1S} I_{1S} - G I_{2S} - \alpha_{1S} - L_{1S} \right] I_{1S} , \quad (1)$$

where G is the Raman gain coefficient for I_{1S}, $\beta_{in\text{-}1S}$ is the nondegenerate TPA coefficient involving one photon at ω_{in} and one photon at ω_{1S}, $\beta_{1S\text{-}1S}$ is the degenerate TPA coefficient involving two photons at ω_{1S}, the GI_{2S} term is the intensity depletion of I_{1S} by pumping I_{2S}, α_{1S} is the OPA coefficient, and L_{1S} is the MDR-related leakage coefficient.

In the case of no TPA, the SRS threshold condition is satisfied when $GI_{in} > \alpha_{1S} + L_{1S}$. I_{1S} builds up exponentially by circulating around the droplet rim until conversion to I_{2S} limits I_{1S}. When TPA is present, the nondegenerate TPA loss ($\beta_{in\text{-}1S}I_{in}I_{1S}$), localized in the region of intense I_{in}, reduces the overall Raman gain to ($G - \beta_{in\text{-}1S}$). In some liquids, G can be less than $\beta_{in\text{-}1S}$. For these liquids, SRS threshold can never be achieved. The degenerate TPA loss ($\beta_{1S\text{-}1S}I_{1S}I_{1S}$) is only important when I_{1S} is strong. Similarly, intensity depletion of I_{1S} by pumping I_{2S} is only important when I_{1S} is strong.

The SRS spectra have been applied to deduce the following physical and chemical properties of a droplet: (1) the droplet size from the spectral spacings of the sharp MDR peaks; (2) the surface tension by forcing the droplet shape to oscillate and by measuring the corresponding spectral oscillations of the sharp MDR peaks; (3) the bulk viscosity by noting how these spectral oscillation amplitudes decay in time; (4) the relative concentration of several dominant species in a multicomponent fuel droplet by calculating the logarithmic ratio of the SRS intensity at the unique Raman shifts of the various species; and (5) the evaporation rate of heated multicomponent

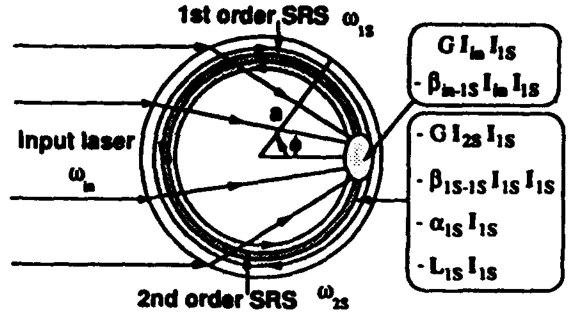

Fig. 3. Schematic of the intensities (shaded areas) and the rays at ω_{in}, ω_{1S}, and ω_{2S} in the droplet equatorial plane. The waves at ω_{1S} and ω_{2S} are represented as two counterpropagating traveling waves within the droplet rim. The Raman gain and various loss mechanisms are indicated.

fuel droplets by noting how the SRS intensity of the evaporating fuel component decreases relative to that of the non-evaporating fuel component. However, accurate determination of the relative concentrations from the relative SRS intensities can only be achieved after we reach a better understanding of both the effect of the losses on the quantum-electrodynamically enhanced Raman gain coefficient and the nonlinear coupling of waves that are on MDR's.

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